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Block Copolymers Containing Monodisperse Segments Produced by Ring-Opening Metathesis of Cyclic Olefins

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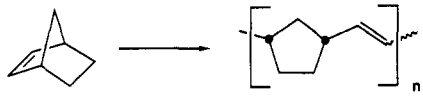
ABSTRACT: Block copolymers (A–B and A–B–A) containing segments of narrow molecular weight distribution (hereafter designated as monodisperse) were synthesized by ring-opening metathesis polymerization using titanacyclobutane **2** as the catalyst. The monomers polymerized were norbornene, benzonorbornadiene, 6-methylbenzonorbornadiene, and *endo*- and *exo*-dicyclopentadiene with the living polymers produced containing up to 50 monomers in each segment. The living polymers were end capped (by a Wittig-type reaction) with acetone and chromatographed to give samples free of catalyst. Three representative examples are the diblocks **35** and **38** with PDI's (polydispersity indices) of 1.08 and 1.14, respectively, and the triblock **36** with a PDI of 1.14. Analysis by differential scanning calorimetry (DSC) showed a single T_g for the block copolymers of polynorbornene and poly(*exo*-dicyclopentadiene), indicating the two polymers are compatible.

Introduction

The study and utilization of block copolymers (both diblock and triblock) has proceeded rapidly since their initial synthesis in the early 1960s.[1] Key to development of this unique and highly useful class of copolymers is the concurrent discovery of living polymerization systems[2] which produced well-defined monodisperse segments of controlled molecular weight. Ring-opening metathesis polymerization (ROMP) is developing into a method of controlled polymerization comparable to known living anionic, cationic, and group transfer systems. To date, the living polymerization of the cyclic olefin norbornene has been reported for titanium,[3] tantalum,[4] and tungsten[5] metathesis systems (eq 1).



(1)

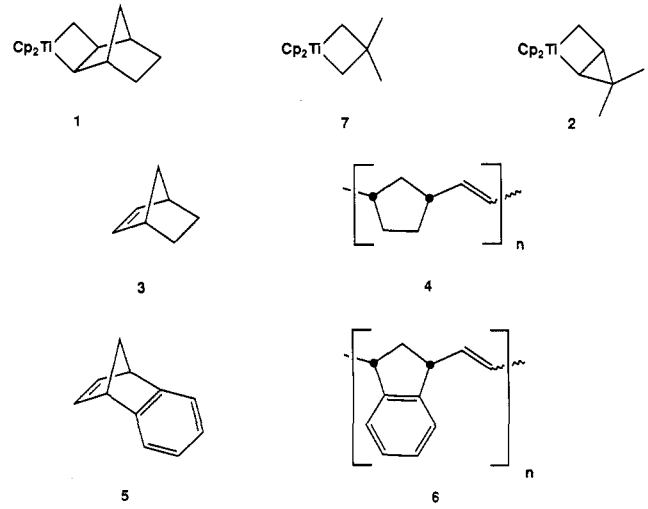
Our research group has extensively studied the olefin metathesis chemistry of titanacyclobutanes[6] and other catalysts. We have applied this knowledge to organic synthesis[7] and in polymer applications have synthesized end-capped polyalkenamers,[8] conducting[9] and rigid[10] polymers, and chelating polyethers.[11] In further developing titanacyclobutanes as highly versatile metathesis polymerization catalysts we are currently exploring their use in block copolymer synthesis. We have previously reported the blocking of norbornene with 3,4-diisopropylidenecyclobutene to give a conducting polymer with improved mechanical properties compared to the parent cyclobutene polymer.[9a]

In this paper we wish to report the results of our investigations into block copolymer synthesis via titanacyclobutanes.

† Contribution no. 7639.

Results and Discussion

Metathesis Polymerization by Titanacyclobutanes. In order to understand the use of titanacyclobutanes in metathesis polymerization a brief review is needed. Gilliom and Grubbs[3] have demonstrated that metallacycles **1** and **2** (derived from norbornene and 3,3-dimethylcyclopropene, respectively) upon reaction with norbornene (**3**) give monodisperse polynorbornene (**4**) (PDI $\simeq$ 1.1) with virtually no chain transfer or termination. The catalyst is active at higher temperatures (≥65 °C), and upon cooling to room temperature the living polymer is stable for several days. If stored at room temperature under an inert atmosphere this system retains some activity even after several months. Rapid decomposition is observed, however, at the polymerization temperature in the absence of monomer.



Initial Studies. In order to synthesize block copolymers, it was necessary to find cyclic olefin monomers other than norbornene that titanacyclobutanes would

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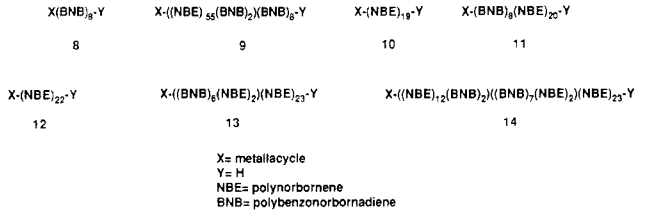
Table I
Block Copolymers of Polynorbornene and Polybenzonorbornadiene Produced by 7[a]

polymer[b]	isolated yield (%)	theor MW	M_n[c]	M_w[c]	PDI[d]
8	84	1330	1550	2810	1.81
9	91	6890	26700	32800	1.23
10	78	2070	6900	12300	1.78
11	77	3350	5250	9420	1.60
12	98	2360	5310	10600	2.30
13	99	2360	6430	14100	2.19
14	96	4950	16200	29100	1.80

[a] See Experimental Section for details of synthesis. [b] The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary VPC) by the equivalents of catalyst present. [c] Determined by gel permeation chromatography vs. polystyrene standards. The polymers 8 and 9 were analyzed a few days after synthesis. The rest of the polymers had decomposed over several months (see text) before analysis. [d] Polydispersity index.

metathesis polymerize to give living systems. Previous work has shown that cyclopentene, although polymerized by **2**, is not a true living system as broader molecular weight dispersities are observed as the polymerization proceeds.[12] The polymerization of benzonorbornadiene (**5**) by WCl_6/Ph_4Sn has been reported to give polybenzonorbornadiene (**6**).[13] The attempted polymerization of 11 equiv of **5** by the metallacycle **7**[14] was complicated by the onset of precipitation of the resulting polymer after 5–6 equiv of monomer had reacted (determined by capillary VPC). Preciptation of the polymer from the reaction mixture (PhMe, 70 °C) completely stopped the polymerization after 9 equiv of **5** were consumed. The isolated sample of polybenzonorbornadiene (polymer **8**, Table I) was only sparingly soluble in organic solvents.



A portion of the living polymer was treated with 60 equiv of norbornene at 70 °C to give the diblock polymer **9**[15] (Table I). During the polymerization, the living polymer redissolved and the rate of polymerization increased. GPC analysis of **9** indicated a large reduction in the polydispersity from the original polymer **8** (Table I). In an attempt to solubilize the polybenzonorbornadiene produced by **7**, a sample of polynorbornene (polymer **10**, Table I) was synthesized first and 13 equiv of benzonorbornadiene (**5**) added. Again the polymerization was stopped by the insolubility of the resulting diblock polymer **11** (Table I). The experiment was repeated with the random copolymerization of norbornene and benzonorbornadiene utilized in hopes of solubilizing the second block. The resulting diblock **13** and triblock **14** (Table I) still had only limited solubilities which hampered the polymerizations. The consumption of monomers throughout the polymerizations and high yields of collected polymer coupled with the observations of increasing molecular weights (GPC) indicate that the diblock and triblock polymers were successfully synthesized. The living polymers described above slowly decomposed over several months at ambient temperature in the drybox to give mostly insoluble yellow solids. GPC analysis (Table I) of the CH_2Cl_2-soluble portion indicated, by broader molecular weight distributions, that the materials had become cross-linked, possibly due to titanium–carbon bond homolysis of the metallacycle end groups followed by radical-initiated cross-linking.

Table II
Block Copolymers of Polynorbornene and Polybenzonorbornadiene Produced by 2[a]

polymer[b]	isolated yield (%)	theor MW	M_n[c]	M_w[c]	PDI[d]
15	42	4460	11300	12100	1.07
16	71	5450	14000	15400	1.10
17	63	9730	27600	33300	1.21
18	561	6340	14900	15900	1.07
19	52	7950	20100	24600	1.22
20	74	4460	10300	11000	1.07
21	62	9260	23500	24700	1.05

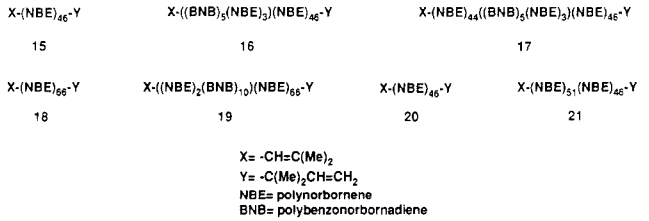
[a] See Experimental Section for details of synthesis. [b] The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary VPC) by the equivalents of catalyst present. [c] Determined by gel permeation chromatography vs polystyrene standards (values not corrected). The correction for polynorborene vs polystyrene is 2.1–2.2. [d] Polydispersity index.

Table III
Ratio of Polynorbornene and Polybenzonorbornadiene in Polymers 15, 16, and 17

polymer	polynorbornene/polybenzonorbornadiene by ^1H NMR[a]	by VPC[b]
15		
16	11.4	9.8
17	18.1	19.6

[a] Determined by integration of the allylic protons of polynorbornene (**4**) vs the allylic protons of polybenzonorbornadiene (**6**). The methylene protons of **6** overlap the allylic protons of **4**, and this was taken into account. [b] Determined by consumption of **3** and **5** during the polymerization (see Experimental Section).

Further Studies. Several steps were taken to improve the synthesis of the block copolymers. Removal of the metallacycle end group, which was deemed necessary in order to stabilize the polymer produced, was accomplished by end capping of the living block copolymers with acetone.[8] The metallacycle **2** that initiates polymerization without an induction period[3] was used instead of **7**. Additionally, the solvent used in the polymerizations was thoroughly deoxygenated and dried by stirring over "titanocene" before use.[16] Under these modified conditions block copolymers were again synthesized. The results for polymers **15–21** are presented in Table II. The isolated



polymers were white amorphous solids that did not decompose over several months in the drybox. Samples exposed to ambient atmosphere, however, turned yellow and became brittle over several weeks.[17]

Further analysis of the polymers **15**, **16**, and **17** (a series of monoblock, diblock, and triblock copolymers) was performed. The rates of polymerization of norbornene in the first and third blocks (**15** and **17**, respectively) were identical, indicating no catalyst decomposition throughout the polymerization. The correct elemental analyses of the three polymers confirmed the purity of the samples isolated after end capping. ^1H NMR analysis gave the ratio

Table IV
Block Copolymers of Polynorbornene, Polybenzonorbornadiene, Poly(1-methylbenzonorbornadiene), Poly(*exo*-dicyclopentadiene), and Poly(*endo*-dicyclopentadiene) Produced by 2[a]

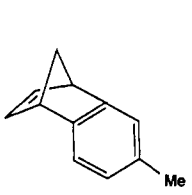
polymer[b]	isolated yield (%)	theor MW	M_n[c]	M_w[c]	PDI[d]
28	75	4740	10200	12100	1.19
29	58	6770	18100	20800	1.15
30	58	6300	15500[e]	17200[e]	1.11[e]
31	90	10700	23900	27400	1.15
32	66	10820	27700	32000	1.16
33	63	15100	46200	58800	1.27
34	96	3200	6840	8290	1.21
35	68	7400	23900	25900	1.08
36	85	13200	43500	49500	1.14
37	78	4400	10500	11200	1.07
38	47	10700	28100	32100	1.14
39	71	6340	*f*	*f*	*f*
40	85	15000	*f*	*f*	*f*

[a] See Experimental Section for details of synthesis. [b] The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary GC) by the equivalents of catalyst present. [c] Determined by gel permeation chromatography vs polystyrene standards (values not corrected). [d] Polydispersity index. [e] A small amount of high molecular weight polymer ($M_n \approx 400{,}000$) was also present and not used to calculate the molecular weight data. [f] Value not determined.

of norbornene and benzonorbornadiene incorporated into each polymer. Comparison of these values with those calculated from the amount of the monomer consumed during the polymerization (by capillary VPC) are presented in Table III. The good agreement of these ratios indicates the assignment of the number of monomer units in each block from consumption of monomer by VPC is a valid approximation.

In testing the improved procedures polynorbornene was blocked with itself (polymers **20** and **21**). Analysis by GPC showed that the polydispersity remained low and the theoretical and experimental molecular weights maintained a constant ratio. The insolubility of polybenzonorbornadiene still presented a problem, though and only short blocks of this polymer could be added before polymerization stopped due to precipitation of the living polymer system from the reaction mixture.

In hopes of producing a more soluble polymer, 6-methylbenzonorbornadiene (**22**) was polymerized by the metallacycle **2**, but the polymer produced (**23**) still became



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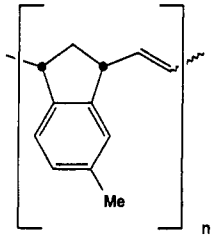

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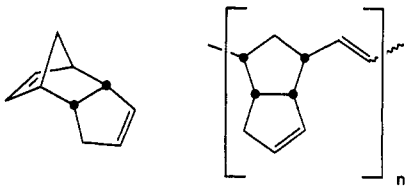
insoluble after 7–9 equiv of monomer were consumed. Two more solutions to the problem were tested. First, one possibility of insoluble polymer formation might be a radical-induced cross-linking (initiated during the polymerization at 70 °C) due to trace amounts of impurities present in the monomer **5** that were not removed by distillation from CaH_2. As a further purification step, therefore, the monomers employed were filtered through alumina several times before further treatment as before. The other solution tested was to examine the polymerization of other monomers besides **5** and **22**. Previous work has shown *endo*-dicyclopentadiene (**24**) can be polymerized by the metallacycles **2** or **7** to give low molecular weight samples of the ring-opened polymer **25**,[18] and therefore this monomer was employed in the next set of experiments. Additionally, *exo*-dicyclopentadiene (**26**) was used in hopes of giving the corresponding polymer **27**.

Table V
Ratio of Polynorbornene to Poly(*exo*-dicyclopentadiene) in Polymers 32, 33, 35, 36, and 38

polymer	polynorbornene/poly(*exo*-dicyclopentadiene) by NMR[a]	by VPC[b]
32	1.2	1.1
33	2.0	2.0
35	2.4	2.0
36	0.79	0.67
38	0.94	0.96

[a] Determined by integration of the aliphatic and olefinic regions of the ^1H NMR spectrum (see Experimental Section). [b] Determined by consumption of 3 and 26 during the polymerization.



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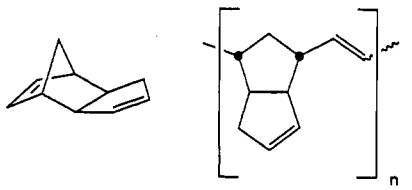

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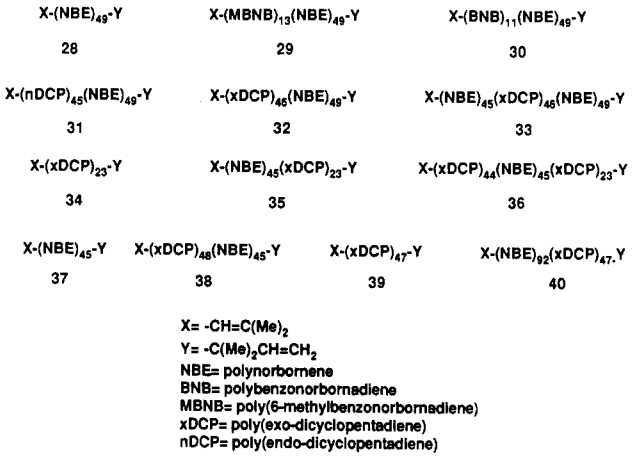
Once again the synthesis of block copolymers was attempted and the results for the isolated polymers **28**–**38** are displayed in Table IV. Polymers **29**–**33** were all



prepared from a sample of polynorbornene (**28**) which was isolated as a living polymer and stored in solution at ambient temperature overnight. The polydispersity of **28** (Table IV) indicated that partial decomposition occurred, presumably induced by metallacycle decomposition,[19] however, the resulting block copolymers produced from **28** were very close to monodisperse. The block copolymerizations of norbornene and benzonorbornadiene

Table VI
The Living Polymerization of *exo*-Dicyclopentadiene (26)[a]

equiv of 26 consumed[b]	% convn[c]	theor MW	M_n[d]	M_w[d]	PDI[e]
16	31	2240	4730	5190	1.10
34	68	4620	10300	11500	1.12
44	89	5940	13800	15200	1.10

[a] See Experimental Section for procedure. [b] Determined by capillary VPC vs an internal standard. [c] Based on 50 equiv of monomer added. [d] Determined by gel permeation chromatography vs polystyrene standards (values not corrected). [e] Polydispersity index.

were still complicated by the insolubility of the resulting block copolymers; therefore, this insolubility is most likely a property of the polymer and not a result of decomposition. The polymers produced from *endo*- and *exo*-dicyclopentadiene were, however, completely soluble, thus permitting the synthesis of blocks containing up to 46 monomer units. ^{1}H NMR was employed as before to determine the ratio of the different monomers incorporated into the block copolymers of polynorbornene and poly(*exo*-dicyclopenatdiene) (Table V). Overlapping of the signals of the two respective blocks complicated the analysis, and an algebraic approximation was used (see Experimental Section). The values are once again in good agreement with the VPC-derived numbers.

The GPC traces of these block copolymers were bimodal, displaying a second smaller peak corresponding to twice the molecular weight of the larger peak. The formation of the smaller fraction would have to occur at either the start or end of the polymerization as constant formation throughout the polymerization would give instead a broader molecular weight distribution. Trace impurities present in either the monomer or catalyst were considered good candidates for cause of the formation of the secondary peak. The monomer **26** was therefore further purified by stirring over sodium at 90 °C for 12 h before distillation. The polymerization of **26** by **2** was repeated, and aliquots were removed at set intervals and analyzed by GPC. The results are presented in Table VI. The GPC traces indicated much less "dimer" present (≤5%), and the lower polydisperties reflect this fact. Further purification of the catalyst and/or monomer or addition of a radical inhibitor may totally eliminate this problem. One important note in the polymerization of **26** is that a plot of percent conversion vs molecular weight (Figure 1) gives a straight line with an intercept of zero, indicating that the polymerization is a living process for this monomer.[2]

Rates of Polymerization of Different Monomers. Previous work has shown that the rate of polymerization of norbornene by titanacyclobutanes is independent of monomer concentration and first-order in catalyst concentration.[3] Although no quantitative kinetic analysis was undertaken in the work reported herein; qualitatively, the polymerizations of benzonorbornadiene, 6-methylbenzonorbornadiene, and *exo*- and *endo*-dicyclopentadiene were similar to above. The rates of polymerization were constant during the synthesis of each block and changed the appropriate amount upon change in the catalyst concentration. Benzonorbornadiene and 6-methylbenzonorbornadiene polymerized at slightly faster rates than norbornene in their respective homopolymerizations and at a comparable rate to norbornene during copolymerizations with norbornene. *exo*-Dicyclopentadiene (**26**) polymerized 5–6 times slower than norbornene (homopolymerizations) and *endo*-dicyclopentadiene (**24**) 15–20 times slower. The rates of the homopolymerizations of norbornene and norbornene derivatives by titanacyclobutanes is determined by the stability of the chain-carrying metallacycles whose decomposition to the carbene controls the rate of polymerization.[3] The data presented above indicate that the metallacycles derived from the respective monomers employed in these studies are comparative in stability as evidenced by similar rates of polymerization.

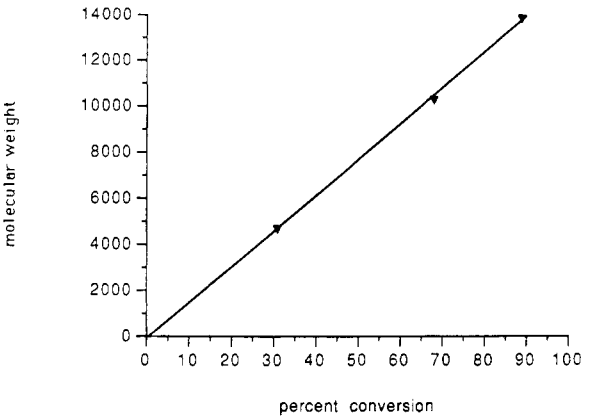


Figure 1. Plot of molecular weight vs percent conversion for the polymerization of *exo*-dicyclopentadiene (**26**). The line was derived from a least-squares fit of the data (correlation = 0.999).

Table VII
T_gs of Block Copolymers of Polynorbornene and Poly(*exo*-dicyclopentadiene)

polymer	% NBE[a]	% xDCP[a]	T_g[b]
36	32	68	79
38	40	60	78
40	58	42	71

[a] Weight percentage of the respective polymer blocks as calculated from the previously determined number ratio (see text). [b] Determined by DSC (heating rate = 20 °C/min).

Morphology of the Block Copolymers. The physical properties of block copolymers lead to desirable characteristics (i.e. elasticity, toughness, processibility) not attainable with the respective homopolymers.[1] In order to determine the morphology of the polymers synthesized in these studies, we analyzed several representative samples by differential scanning calorimetry (DSC). Samples of polynorbornene (polymers **15**, **18**, **21**, and **37**; M_n = 10 500–23 500 vs polystyrene) showed a single T_g of 30–38 °C, generally increasing with higher molecular weights. In contrast, a sample of poly(*exo*-dicyclopentadiene) (M_n = 13 800 vs polystyrene) showed a T_g of 103 °C (after brief annealing at 200 °C). The higher T_g of poly(*exo*-dicyclopentadiene) compared to polynorbornene is most likely due to the more rigid nature of bicyclic rings present in the former. The block copolymers of polynorbornene and poly(*exo*-dicyclopentadiene) analyzed (**36**, **38**, and **40**) gave only a single T_g, intermediate between the T_gs of the respective homopolymers (Table VII). This implies true compatibility of the two polymers that has only been observed in a few instances for other systems.[1] Block copolymers of polynorbornene and polybenzonorbornadiene, containing a small fraction of polybenzonorbornadiene, also showed only one T_g (**16**, T_g = 47 °C; **17**, T_g = 49 °C; **29**, T_g = 42 °C).

Conclusion

The synthesis of block copolymers by metathesis polymerization of cyclic olefins with titanacyclobutanes has been achieved. The use of blocks which remain in solution throughout the polymerization permits the synthesis of polymers containing 50 monomer units in each segment. Impurities present in the monomer and/or catalyst which

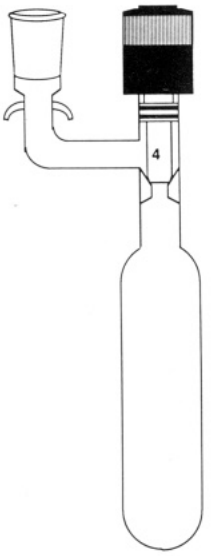


Figure 2. Design of heavy-walled glass tubes used for polymerizations (actual size reduced 40%).

cause the formation of secondary peaks in the GPC traces can be removed to give block copolymers containing essentially monodisperse segments. Finally, block copolymers of polynorbornene and poly(*exo*-dicyclopentadiene) exhibit a single T_g, indicating the two polymers are compatible.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed by using standard high-vacuum or Schlenk techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular seives and a Vacuum Atmospheres drybox under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C) and a JEOL GX-400 (399.65 MHz ^1H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvents. Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator (column: 0.24 mm × 15 m DBI). High vacuum evacuation of samples were performed at 10^{-5} Torr. Elemental analysis was performed by L. Henling at the analytical facilities of the California Institute of Technology.

Gel permeation chromatographic (GPC) analyses utilized Shodexx KF-803, 804, 805, and 805.5 columns, a Spectroflow 757 absorbance detector (λ = 254 nm), and a Knauer differential refractometer. GPC analyses were performed on 0.20 or 0.40% w/v solutions of polymer in CH_2Cl_2. Typically, an injection volume of 0.100 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from MW = 3550 to 600 000 (correction factors of 2.1–2.2 have been demonstrated for norborene and derivatives in the past.[3] The molecular weight averages and distribution was calculated by standard procedures[20] from the refractive index trace and were not corrected for peak broadening. Transition temperatures were determined under a nitrogen atmosphere on a Perkin-Elmer Delta Series DSC 7 at a heating rate of 20 °C/min unless otherwise noted. Oil bath temperatures for all polymerizations were maintained by use of an I^2R Thermo-O-Watch, Model L6-1000SS. Polymerizations were carried out in heavy-walled glass tubes equipped with a stir bar, female 14/20 joint, and a Teflon valve (see Figure 2).

Materials. The metallacycles **2**[3] and and **7**[6c] were prepared as previously described. The cyclic olefin, 3,3-dimethylcyclopropene (used to synthesize **2**), was kindly provided by S. C. Virgil. The monomers used in the polymerizations were prepared and purified as follows. Norbornene was purchased from Aldrich, refluxed over sodium, and distilled prior to use. Benzonorbornadiene (**5**) and 6-methylbenzonorbornadiene (**22**) were prepared by the method of Wittig and Knauss[21] and originally purified by vacuum distillation from CaH_2. In later experiments (see synthesis of polymers **28–38**) the monomers were filtered through alumina, stirred over CaH_2 overnight, and then vacuum-distilled from CaH_2. Pure *endo*-dicyclopentadiene **24** was synthesized by allowing freshly prepared cyclopentadiene to dimerize at 0 °C over a 2-month period (82% conversion),[22] removing the unreacted cyclopentadiene by rotary evaporation, and vacuum distillation of the product from CaH_2. In later experiments it was further purified as above. *exo*-Dicyclopentadiene (**26**) (95% exo, 5% endo) was purchased from Wiley Organics and purified as above. In the last set of experiments (see text) the monomer was stirred over sodium at 90 °C overnight and then vacuum-distilled from sodium. All monomers listed above were deoxygenated by three freeze–pump–thaw degassing cycles and stored in the drybox or in tubes equipped with Teflon valves. Octane and *p*-xylene (used for VPC internal standards) were distilled from CaH_2 and deoxygenated as above before use. BHT was purchased from Aldrich (Gold Label).

Toluene was dried (CaH_2), transferred to sodium benzophenone ketyl, and later distilled into a solvent flask equipped with a Teflon screw-type valve. In later experiments, the toluene was further purified by stirring prepurified material (distilled from sodium benzophenone ketyl) over "titanocene"[16] overnight and then vacuum transferring into a flask equipped with a Teflon valve. Benzene-d_6 (Merck, Sharp & Dohme) was transferred to sodium benzophenone ketyl, later distilled, and stored in the drybox. Methanol for precipitation of polymers was reagant grade and used without further purification.

Polymerization of Benzonorbornadiene (5) by 7. The metallacycle **7** (0.020 g, 0.081 mmol) was dissolved in 0.4 mL of C_6D_6 in an NMR tube and **5** (0.012 g, 0.081 mmol) added by syringe. After 40 min ^1H and ^{13}C NMR spectra were recorded which indicated quantitative formation of isobutylene and the new metallacycle derived from Cp2Ti=CH_2 and **17**: ^1H NMR (C_6D_6) δ 7.14 (m, 4 H), 5.50 (s, 5 H), 5.18 (s, 5 H), 3.36 (d, J = 9.0 Hz, 1 H), 3.11 (b s, 1 H), 2.84 (dd, J_1 = 9.3 Hz, J_2 = 8.8 Hz), 1.88 (pt, J_1 = 8.8 Hz, J_2 = 8.8 Hz, 1 H), 0.34 (pq, J_1 = 9.0 Hz, J_2 = 9.3 Hz, J_3 = 8.8 hZ); ^{13}C NMR (C_6D_6) δ 153.1, 148.7, 125.9, 124.6, 121.6, 118.8, 110.3, 109.5, 103.7, 74.2, 53.8, 49.3, 45.1, 19.1 (the spectra are similar to that for metallacycle **1** derived from norbornene: see ref 18, p 85).

To the metallacycle generated above was added an additional 6 equiv of **5** by syringe. The NMR tube was heated at 70 °C in the NMR probe and consumption of the monomer observed with the appearance of polymer peaks at δ 7.20 (m), 5.95 (b s), 5.75 (b s), 4.15 (b s), and 3.75 (b s), 2.68 (b s), and 1.80 (b s). After approximately 5 equiv monomer was consumed, the polymerization stopped. The contents of the tube was dark red-brown with a pink precipitate.

Synthesis of 8. A stock solution of **5** (2.237 g, 15.7 mmol) was prepared with 0.2 mL of octane (internal VPC standard) and additional PhMe to give 25.00 mL total volume ([5] = 0.63 M). The metallacycle **7** (0.045 g, 0.18 mmol) and 3.0 mL of stock solution (0.268 g, 1.89 mmol, 11 eq of 5) were combined in a vial in the dry box and transferred by pipette to a glass tube. The tube was brought out of the dry box and attached to a hose on the vacuum line via the joint. The deep red mixture was stirred 0.5 h and the isobutylene produced by reaction of **7** with **5** was removed by three freeze-pump-thaw degassing cycles.

Stirring was continued at 67–68 °C in an oil bath. Samples were withdrawn periodically by dipping an oven-dried pipette (purged with argon) into the polymerization solution under a stream of argon. The small amount retained in the tip of the pipette by capillary action was diluted with acetone to precipitate by polymer and the supernatant analyzed by VPC. The ratio of **5** to octane was used to determine the eq of 5 remaining. A fine precipitate began to form 20 min after the start of the polymerization and more appeared as the polymerization proceeded. After 50 min at the polymerization temperature (9 equiv of **5** consumed), the tube was allowed to cool to room temperature, freeze–pump–thaw degassed and transferred to the drybox. The solution (1.0 mL) was removed to a vial, the vial was brought out, and its contents were added to stirring MeOH to precipitate **8** (0.067 g, 84% yield based upon percent completion) as a fine pink powder. The polymer was analyzed by GPC (see Table I) and NMR: ^1H NMR ($CDCl_3$) δ 7.15 (b s, 4 H), 5.75 (b s), 5.65 (b s,

2 H), 4.21 (b s), 3.79 (b s, 2 H), 2.68 (b s), 1.84 (b s, 2 H); ^{13}C NMR ($CDCl_3$) δ 146, 134, 133, 127, 124, 123.5, 48, 43. The ^1H and ^{13}C NMR spectra were consistent to those reported in the literature.[13]

Synthesis of the Diblock Polymer 9. A stock solution of norbornene in toluene with an internal standard of octane was prepared as before. To the remaining mixture from the synthesis of **8** consisting of the living polymer (0.160 g, 0.12 mmol) and **5** (0.037 g, 0.26 mmol, 2.2 equiv/Ti) in PhMe (2.0-mL total volume) was added 4.0 mL of the stock norbornene solution (0.685 g, 7.27 mmol, 61 equiv/Ti of norbornene). The polymerization was performed as before. The precipitate originally present disappeared as the polymerization progressed. After 15.5 h (57 equiv of norbornene and 2 equiv of benzonorbornadiene consumed by VPC) the tube was allowed to cool to room temperature. The polymer **9** (0.756 g, 79% yield) was collected as before and analyzed by GPC (see Table I).

Synthesis of Polymers 10–14. These polymers were synthesized by the same procedure listed for the polymers **8** and **9**. The results are presented in Table I.

Synthesis of Polymers 15–21. The method used for polymerization and isolation of the resulting polymers was modified from before as follows.

The toluene was further dried (see Materials). The metallacycle **2** was employed instead of **7**. The polymerizations were performed at 71–72 °C. The polymers produced were end capped with acetone and purified by flash chromatography on silica gel. A typical end-capping and isolation procedure for polymer **15** is given below.

To a tube equipped with a Teflon valve and containing a solution of living polynorbornene (0.211 g, 0.046 mmol, 46 equiv of norbornene/chain) in toluene (1.0-mL total volume) was added 0.1 mL (0.079 g, 1.36 mmol, 30 equiv/Ti) of acetone by syringe. The resulting mixture was stirred at 71 °C for 15 min to give a clear pale orange solution. The mixture was allowed to cool, diluted with PhMe, and filtered through a pad a silica gel with suction. The pad was liberally washed with PhMe, and the combined filtrate and washings were reduced in volume by rotary evaporation to approximately 2 mL. The resulting PhMe solution of product was added dropwise to a stirring MeOH solution to precipitate the polymer. The pure white amorphous solid was dried under high vacuum overnight.

The polymers **15**, **16** and **17** were submitted for elemental analysis. Anal. Calcd for $C_4H_7(C_7H_{10})_{46}C_5H_9$ (**15**): C, 89.23; H, 10.77. Found: C, 89.10; H, 10.55 (no detectable ash). Anal. Calcd for $C_4H_7(C_{11}H_{10})_5(C_7H_{10})_3(C_7H_{10})_{46}C_5H_9$ (**16**): C, 89.71; H, 10.29. Found: C, 89.31; H, 10.29 (no detectable ash). Anal. Calcd for $C_4H_7(C_7H_{10})_{44}(C_{11}H_{10})_5(C_7H_{10})_3(C_7H_{10})_{46}C_5H_9$ (**17**): C, 89.58; H, 10.42. Found: C, 89.40; H, 10.23 (no detectable ash).

Polymerization of 6-Methylbenzonorbornadiene (22). The polymerization was performed by the same procedure as for **15–21** except the isolated polymer was not end capped. The product was a fine pink solid that was only sparingly soluble in PhMe or CH_2Cl_2. GPC analysis gave M_n = 3590, M_w = 6330, and PDI = 1.76. The polymer was also analyzed by NMR: ^1H NMR ($CDCl_3$) δ 7.15 (m, 3 H), 5.70 (b s), 5.52 (b s 2 H), 4.15 (b s), 3.85 (b s, 2 H), 2.65 (b s), 1.80 (b s, 2 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 146, 143, 136, 133, 127, 124.5, 123.5, 48, 43, 22.

Living Polymerization of *exo*-Dicyclopentadiene (26). The polymerization was performed as above with the metallacycle **2** (0.017 g, 0.065 mmol) and **26** (0.430 g, 3.25 mmol, 50 equiv) in PhMe (2.0-mL total volume). At set intervals during the polymerization aliquots of the mixture were removed and end capped with acetone and the isolated polymers analyzed by GPC (see Table VI).

Synthesis of Polymers 28–38. These polymers were synthesized by the same procedure as used for polymers **15–21**. The monomers were more thoroughly purified as described in the Materials. The polymerization temperature was increased to 75 °C.

NMR Determination of the Ratio of Homopolymers in Block Copolymers 32, 33, 36, and 37 (Table V). The overlap of the ^1H NMR of polynorbornene and poly(dicyclopentadiene) prevented a simple integration to determine the ratio of the polymers present. An algebraic approximation was used instead as follows. The olefinic region of the NMR was modeled as arising from two olefinic protons per monomer unit of polynorbornene and four olefinic protons per monomer unit of poly(dicyclopentadiene). Similarly the aliphatic region was modeled as arising from eight protons each per monomer unit of polynorbornene and poly(dicyclopentadiene), respectively. These relationships are given in eq 2 and 3.

$$2x + 4y = (\text{olefinic protons})z \quad (2)$$

$$8x + 8y = (\text{aliphatic protons})z \quad (3)$$

Solving these two equations in three unknowns (x, y, z) yields an expression for the ratio of polynorbornene to poly(dicyclopentadiene) present in the block copolymers as given in eq 4.

$$\frac{x}{y} = \frac{2(\text{aliphatic}) - 4(\text{olefinic})}{4(\text{olefinic}) - (\text{aliphatic})} \quad (4)$$

x = monomer units of polynorbornene;

y = monomer units of polydicyclopentadiene;

z = correction factor of integration to actual number of protons

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Registry No. **2**, 99798-41-1; **5**, 56842-50-3; **7**, 80122-07-2; **9**, 114397-36-3; **22**, 114397-37-4; **26**, 25704-32-9; **29**, 114397-38-5; **31**, 114488-36-7; **32**, 114488-37-8.

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The isobutylene was removed by freeze–pump–thaw degassing before the polymerization was started (see the Experimental Section).
(15) The second block contained a small amount of polybenzonorbornadiene due to residual monomer present from the previous block. Typically the blocks synthesized contained a minor amount of the other polymer. The living polymer decomposes in the absence of monomer at 70 °C. Therefore, the polymerizations were run to 95% completion.
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Synthesis and Properties of Segmented and Block Poly(hydroxy ether–siloxane) Copolymers

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ABSTRACT: Segmented or block poly(hydroxy ether–siloxane) copolymers that are both chemically cross-linked and microphase separated have been synthesized. In this work, the molecular weight of the siloxane block lengths varied from 900 to 12 400 g/mol, and the hydroxy ether block lengths varied from 340 to 3700 g/mol. Calorimetric, dynamic mechanical, and small-angle X-ray scattering measurements showed that higher block length oligomers gave networks with a more well-defined two-phase morphology. The mechanical behavior of the networks depended on the continuous phase with ultimate elongations ranging from 50 to 180% and moduli ranging from 1.0 to 600 MPa.

Introduction

Organosiloxane-based elastomers have many desirable properties including low-temperature flexibility, thermal and oxidative stability, low surface energy, high compressibility, and high gas permeability. Consequently, these elastomers have been used widely. These materials have a low glass transition temperature, T_g, (ca. −123 °C), and at room temperature, the molecular segments are sufficiently mobile such that cracks readily initiate and propagate.[1] The low melting point (−40 °C), however, prevents strain-induced crystallization,[2-4] which leads to reduced toughness.

Particulate fillers are commonly used to increase the toughness. Reinforcement may also be achieved by preparing model networks containing both long and short chains.[5-7] These bimodal networks showed enhanced tensile strength as the fraction of short chains is increased. Haidar and Smith[8] have shown that the tensile strength and relaxation rate pass through a maximum between 30 and 40% by weight short chains. The increased relaxation rate results from decreased chain mobility. Thus, reinforcement may also be achieved by increasing the viscoelastic response of the network.

The synthesis of multiphase systems in the form of block, graft, or segmented copolymers is a viable alternative in the design of elastomeric materials with good mechanical properties.[9-11] Generally, these materials are composed of hard and soft segments or blocks. The morphology of these elastomers will depend on the relative molecular weights of the individual blocks, whereas the segmental interactions will control the phase purity. Smith[12-14] has investigated the mechanical properties of several segmented and block copolymers. The hard segment domains in these elastomeric systems were found to impede the formation of and slow the growth of microcracks as well as prevent cracks from attaining a critical size where they become unstable. Furthermore, the incorporation of a second phase serves to increase the internal viscosity, distributing the stress more uniformly throughout the specimen, thereby reducing stress concentrations.

Segmented or block copolymers containing a sufficient concentration of a hard component whose T_g is well above the test temperature are more effective in imparting strength than particulate fillers since the domains are dispersed uniformly and can undergo deformation. Block copolymers of siloxane with poly(arylene ether sulfones),[15,16] poly(arylene esters),[17,18] polycarbonates,[19-21] and other hard segments[9] are classic examples of single-component, microphase-separated polymers. These are typically prepared by the condensation of silylamine-terminated siloxane oligomers with phenolic hydroxyl-terminated hard blocks affording a perfectly alternating $(A–B)_n$ structure. Microphase separation is found provided sufficiently long block lengths are used and the mechanical response is dominated by the continuous phase.[16,22] McGrath and co-workers[25,26] have recently reported a series of segmented copolymers prepared by an oligomer–monomer synthetic approach. The linkage between the blocks is formed simultaneously with the growth of the second block, where the nature of the linkage depends upon the functional end groups of the preformed oligomer and monomer. This synthetic route is similar to the preparation of Hytrel polyurethane and Estane urea-linked copolymers. A series of novel siloxane–imide, siloxane–hydroxy ether,[24] and siloxane–urea[23,26] copolymers were prepared, where apparent strong intermolecualr interactions within the hard segment provided microphase-sep-

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